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(19)

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(54) IMPROVEMENTS IN OR RELATING TO A METHOD OF BONDING ALUMINA TO A REFRACTORY METAL OR ALLOY

(71) We, THE GENERAL ELECTRIC COMPANY LIMITED, of 1 Stanhope Gate, London, W1A 1EH, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of bonding alumina to a refractory metal or alloy, and more particularly to a method of hermetically bonding an alumina component to a component of a refractory metal or alloy having thermal expansion characteristics substantially matching those of the alumina component. It is to be understood that the term "alumina component" is used herein, for brevity, to refer to a component formed either of a refractory oxide ceramic material having a high alumina content, exceeding 85% by weight, or of crystalline material composed of substantially pure alumina. The invention is also concerned with composite articles comprising an alumina component and a refractory metal or alloy component hermetically bonded together by the method described, and with electrical devices incorporating in their construction a composite article of this kind.

The invention is especially concerned with the hermetic closure of electric discharge device envelopes formed of a said ceramic or crystalline alumina material, by sealing refractory metal or alloy closure members around apertures in the envelopes, for example over the ends of tubular envelopes. One particular device with which the invention is concerned is an electric discharge lamp of the type, usually referred to as a high pressure sodium vapour electric discharge lamp, comprising a tubular discharge envelope formed of light-transmissive alumina, either in the form of sintered polycrystalline alumina which may contain a small proportion, for example 1% by weight, of other refractory oxides such as magnesia, or in the form of crystalline corundum, such alumina materials being resistant to attack by hot sodium vapour. The alumina envelope has a filling of sodium, rare gas, and usually at least one additional metal, especially mercury, in quantities such that in operation of the lamp a pressure exceeding about 400 torr is developed, and the envelope is closed at both ends by closure members of a refractory metal or alloy having thermal expansion characteristics substantially matching those of the alumina of the tube, and also resistant to sodium vapour attack, for example niobium or a niobium-based alloy. It has been proposed to seal such closure members to the ends of the alumina tube by means of a calcium aluminate glass having thermal expansion characteristics substantially matching those of the materials of the tube and closure members, but difficulty is sometimes experienced in achieving a satisfactory strong hermetic bond between such glass and the refractory metal, in particular niobium, the seals tending to fracture in operation of the lamp. Moreover the bond between the sealing glass and the niobium has been found to be vulnerable to attack by liquid sodium present in the vicinity of the end caps of the lamp, so that special arrangements have to be made to avoid contact between liquid sodium and the seals.

It is an object of the present invention to provide an improved method of bonding together components of refractory metal or alloy and high alumina content ceramic material, or crystalline alumina, of substantially matching thermal expansion characteristics, a particular object being the provision of an improved method of sealing niobium end caps to crystalline or ceramic alumina tubes, in the manufacture of high pressure sodium vapour discharge lamps, whereby the above-mentioned difficulty can be reduced or overcome.

According to the invention, a method of hermetically bonding an alumina component, as hereinbefore defined, to a component formed of a refractory metal or alloy having thermal expansion characteristics substantially matching, as hereinafter defined, those of the alumina component, includes the steps of forming a continuous, adherent coating of substantially oxygen-free metallic tungsten on that surface of the metal or alloy component which is to be bonded to the alumina component, assembling the metal or alloy component and the alumina components together with a layer of calcium aluminate sealing glass interposed between the tungsten-coated surface of the metal or alloy component and the mating surface of the alumina component, and pressing the assembly of said components and glass layer together while simultaneously heating the assembly in an inert atmosphere or in vacuum to a temperature sufficiently high to cause the glass layer to melt and bond to both the surface of the alumina components and the tungsten coating on the metal or alloy component.

The expression "substantially matching", as used herein with reference to the thermal expansion characteristics of the metal and alumina components is to be understood to mean that the said characteristics of the parts concerned are sufficiently similar to prevent the occurrence of strain or damage to the components, or cracking of the seal, as a result of differential expansion when the sealed components are heated to high temperatures in use.

We have found that the presence of oxygen in the tungsten coating formed on the metal or alloy component is undesirable since it reduces the ductility of the tungsten coating and also diffuses into the underlying metal, resulting in embrittlement of the latter, especially in the case of niobium: these effects mitigate against the formation of a satisfactory seal between the tungsten-coated metal or alloy component and the alumina component. It has therefore been stipulated, above, that the tungsten is substantially oxygen-free, by which is meant that oxygen either is completely absent, or is present in such a small proportion that no detectable embrittlement of the underlying metal results.

We have found that strong hermetic seals can readily be formed between high alumina content ceramic material, or crystalline alumina, and a refractory metal or alloy of substantially matching thermal expansion characteristics, especially niobium or a niobium-based alloy, by the method of the invention and that these seals are not susceptible to attack by hot alkali metal vapour or liquid alkali metal. Hence this method is particularly advantageous for sealing niobium end closure members to the ends of alumina tubes, in the manufacture of high pressure sodium lamps as aforesaid, enabling a simple construction of the lamp envelope-end closure assembly to be employed, without the necessity of incorporating any special arrangement for preventing the seal from coming into contact with liquid sodium.

The tungsten coating is suitably formed on the refractory metal or alloy component surface by deposition from the vapour phase, the vapour of a tungsten compound decomposable by heat to liberate metallic tungsten being brought into contact with the metal surface, heated to the decomposition temperature of the said compound, under such conditions that the liberated tungsten is deposited on the component surface is a substantially oxygen-free state. A preferred tungsten compound for use for this process is tungsten hexacarbonyl, which is decomposed, with liberation of metallic tungsten, on coming into contact with the metal or alloy component surface heated to 700°C. The metal surface is preferably roughened, for example by etching, before exposure to the vapour of a tungsten compound, to ensure satisfactory adhesion of the tungsten coating to the surface.

Alternatively, the tungsten coating may be applied to the surface of the metal or alloy component by an appropriate plating technique, from the liquid phase.

The tungsten coating should not be sufficiently thick to have any appreciable effect on the thermal expansion characteristics of the metal or alloy component: a suitable thickness is from 1 to 5×10^{-4} inch, an oxygen-free coating of such thickness being sufficiently ductile to accommodate the difference between the thermal expansion coefficients of the tungsten coating and the substrate metal.

The calcium aluminate sealing glass referred to herein is of the kind known to be suitable for sealing high alumina content ceramic material to metals of matching expansion, consisting essentially of alumina and calcium oxide with optional minor additions of one or more other oxides such as magnesium oxide, strontium oxide, barium oxide and boric oxide, and free from silica, the composition being adjusted as required to give a glass having thermal expansion characteristics substantially matching those of the ceramic and metal or alloy components to be sealed together.

The glass sealing layer may be introduced between the mating alumina and tungsten-coated metal surface in the form of glass powder, provided that one of the said surfaces is suitably shaped to retain powder: for example, in the manufacture of a high pressure sodium discharge lamp, the niobium end closure members may be provided with flanges bent to form annular channels which can contain powder and into which the ends of the alumina tube can be inserted, as described in the specification of co-pending Patent Application No. 60228/70 (Serial

No. 1,318,658). Alternatively the sealing layer may be introduced as a preformed glass shim or washer, which can be inserted between two plane surfaces to be sealed together.

A specific method in accordance with the invention, which we have carried out in the manufacture of a high pressure sodium vapour electric discharge lamp having a tubular polycrystalline alumina discharge envelope closed at both ends by niobium caps, will now be described by way of example, with reference to the drawing accompanying the Provisional Specification, which shows the completed lamp in part-sectional elevation.

Referring to the drawing, the discharge envelope 1, formed of light-transmissive sintered polycrystalline alumina containing 1% by weight of magnesium oxide, is closed at both ends by caps 2, 3, formed from niobium sheet and comprising cylindrical portions 4, 5, closed at the inner ends, inserted within the tube 1, and having at the outer ends flanges with outwardly inclined portions forming annular channels, 6, 7, into which the ends of the alumina tube 1 are sealed by the method of the invention: the dimensions of the flanges and seals are exaggerated in the drawing, for clarity. The lamp electrodes, 8 and 9, in the form of silicated tungsten rods each with a tungsten wire coil, retaining a small quantity of activator material, wound on the inner end, are respectively carried by the closed inner ends of the cap cylinders 4 and 5. The cylinder 4 also carries a niobium connection tap 10, the electrode 8 and the tag 10 being brazed respectively to the inner and outer sides of the inner end of the cylinder. The electrode 9 is attached to the inner end of a niobium exhaust tube 11 which is brazed to, and extends through an aperture in, the inner end of the cylinder 5: the inner end of the tube 11 is pinched into and brazed to a recess in the electrode 9, small spaces being left between the tube and the electrode to provide ducts for communication of the tube 11 with the interior of the lamp envelope.

In the manufacture of the lamp described above with reference to the drawing, for forming the seals between the alumina tube 1 and the niobium caps 2, 3, the interior surfaces of the caps, including the interior surfaces of the channels 6, 7, are first plated with tungsten metal, as shown at 12, 13: it will of course be understood that it is only necessary to plate the channel surfaces, but it would be inconvenient to mask the remainder of the cap surfaces during the plating process, and the presence of a tungsten coating on the cylindrical and inner end portions of the caps is immaterial. It is most convenient, in the production of lamps in quantity, to plate one side of a niobium sheet before the individual caps are made therefrom. The niobium surface to be plated is first prepared by etching with hydrofluoric acid and nitric acid, and the niobium sheet (or preformed caps) is (or are) then heated to 700°C in vacuum; tungsten hexacarbonyl is evaporated in vacuum at a temperature of 25—30°C, to give vapour at a pressure of 0.01 to 0.001 torr, which is passed over the heated niobium surface, suitably for 2 hours to give an adherent tungsten coating 2×10^{-4} inch thick on the niobium.

The electrodes, connection tag and exhaust tube are attached to the tungsten-plated niobium caps, as shown in the drawing, titanium being employed for forming all the brazed joints referred to (if desired, the tag and exhaust tube can be attached to the respective preformed caps before plating the latter). Sealing layers, for sealing the ends of the alumina tube to the tungsten-plated caps, are then formed by introducing into the channels 6 and 7 a quantity of glass powder of composition, in molar percentages, 33.1% alumina, 51.4% calcium oxide, 9.5% magnesium oxide, 4.2% barium oxide and 1.8% boric oxide, mixed with water to form a thick slurry, heating the caps to 1350°C in vacuum or argon to melt the glass, and cooling to form a solidified layer of glass, as shown at 14, 15 in the drawing.

The cap assemblies, with the glass sealing layers formed in the troughs as described above, are placed over the respective ends of the alumina tube, and the whole assembly is supported vertically in a closed vessel, with a pressure of 10 Kg applied to the flange of the uppermost cap, and heated in vacuum or argon so that the temperature is raised to 1500°C. in about ten minutes, then allowed to cool while the pressure is maintained. As a result of this treatment, the ends of the alumina tube is firmly embedded in and bonded to the glass layers 14 and 15, and the latter are bonded to the tungsten coatings in the channels 6 and 7.

The manufacture of the lamp is completed by evacuating the envelope and introducing a filling of sodium, mercury and rare gas, for example xenon at a pressure of 30 torr, through the tube 11, and finally sealing the tube 11 by pinching and welding.

In a specific example of a lamp of the form described above with reference to the drawing, the tube 1 was 120 mm long and had an internal diameter of 7.5 mm, with a wall thickness of 0.8 mm. Each of the cap cylinders 4, 5 was slightly less than 7.5 mm in external diameter and 2.5 mm long, and had a flange formed so as to give a channel 6, 7 having an internal width of 1.0 mm and depth of 0.5 mm. The electrodes 8 and 9 were both 1.0 mm in diameter and 12 mm long, 3 mm of the length of the exhaust tube 11 extending within the envelope constituting part of the length of the electrode 9.

The lamp shown in the drawing is mounted coaxially within a cylindrical glass outer

jacket designed to maintain the envelope 1 at a suitable high temperature when the lamp is in operation, and electric current supply leads are connected to the lamp electrodes by being attached to the niobium tag 10 and the exhaust tube 11 respectively. The outer jacket, lamp mounting means, and leads are all of well known form, and have therefore been omitted from the drawing for simplicity.

In a modification of the above example, the tube constituting the lamp envelope may be formed of transparent crystalline corundum, the tube consisting of either a single crystal or a few large crystals of corundum. The niobium end caps are sealed to such a tube by the method described in the example for sealing the end caps to a sintered polycrystalline alumina tube.

WHAT WE CLAIM IS:—

1. A method of hermetically bonding an alumina component, as hereinbefore defined, to a component formed of a refractory metal or alloy having thermal expansion characteristics substantially matching, as hereinbefore defined, those of the alumina component, which method includes the steps of forming a continuous, adherent coating of substantially oxygen-free tungsten on that surface of the metal or alloy component which is to be bonded to the alumina component, assembling the metal or alloy component and the alumina component together with a layer of calcium aluminate sealing glass interposed between the tungsten-coated surface of the metal or alloy component and the mating surface of the alumina component, and pressing the assembly of said components and glass layer together while simultaneously heating the assembly in an inert atmosphere or in vacuum to a temperature sufficiently high to cause the glass layer to melt and bond to both the surface of the alumina component and the tungsten coating on the metal or alloy component.

2. The method according to Claim 1, wherein the said refractory metal or alloy component is formed of niobium or a niobium-based alloy.

3. The method according to Claim 1 or 2, wherein the tungsten coating is formed on the surface of the refractory metal or alloy component by bringing the vapour of a tungsten compound, which is decomposable by heat to liberate metallic tungsten, into contact with the surface of said component, heated to the decomposition temperature of said compound, under such conditions that the liberated tungsten is deposited on said surface in a substantially oxygen-free state.

4. The method according to Claim 3, wherein the said decomposable tungsten compound is tungsten hexacarbonyl, and the surface of the refractory metal or alloy component is heated to 700°C.

5. The method according to any preceding Claim, wherein the tungsten coating on the refractory metal or alloy component is from 1 to 5×10^{-4} inch thick.

6. The method according to any preceding Claim, wherein the sealing glass layer is introduced between the mating surfaces of the alumina component and the tungsten-coated metal or alloy component in the form of glass powder, one of said surfaces being suitably shaped to retain powder.

7. The method according to any one of the preceding Claims 1 to 5, wherein the sealing glass layer is introduced between the mating surfaces of the alumina component and the tungsten-coated metal or alloy component in the form of a preformed glass shim or washer.

8. A composite article comprising an alumina component, as hereinbefore defined, and a component formed of a refractory metal or alloy having thermal expansion characteristics substantially matching those of the alumina component, wherein the said components have been hermetically bonded together by a method according to any one of the preceding Claims.

9. An electrical device incorporating in its construction a composite article according to Claim 8.

10. A high pressure sodium vapour electric discharge lamp having a tubular discharge envelope, which constitutes an alumina component, as hereinbefore defined, closed at both ends by niobium closure members, wherein the closure members have been sealed to the ends of the discharge envelope by a method according to any one of the preceding Claims 2 to 7.

11. A method of manufacturing a high pressure sodium vapour electric discharge lamp, which includes the step of sealing niobium end caps to an alumina discharge envelope by the method according to Claim 2, and which is carried out substantially as hereinbefore described by way of example.

12. A high pressure sodium vapour electric discharge lamp, substantially as shown in, and as hereinbefore described with reference to, the drawing accompanying the Provisional Specification, and manufactured by the method according to Claim 11.

For the Applicants,
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1361225 PROVISIONAL SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*